

LLDPE/LDPE Blends. I. Rheological, Thermal, and Mechanical Properties

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ABSTRACT: Structure and mechanical properties were studied for the binary blends of a linear low density polyethylene (LLDPE) (ethylene-1-hexene copolymer; density = 900 kg m^{-3}) with narrow short chain branching distribution and a low density polyethylene (LDPE) which is characterized by the long chain branches. It was found by the rheological measurements that the LLDPE and the LDPE are miscible in the molten state. The steady-state rheological properties of the blends can be predicted using oscillatory shear moduli. Furthermore, the crystallization temperature of LDPE is higher than that of the LLDPE and is found to act as a nucleating agent for the crystallization of the LLDPE. Consequently, the melting temperature, degree of crystallinity, and hardness of the blend increase rapidly with increases in the LDPE content in the blend, even though the amount of the LDPE in the blend is small. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3153–3159, 1999

Key words: linear low density polyethylene; low density polyethylene; polymer blend; rheological property; crystallization

INTRODUCTION

Blends of linear low density polyethylene (LLDPE) and low density polyethylene (LDPE) are often used for film manufacture because of their good processability and excellent mechanical properties. Furthermore, various properties of the blends, such as rheological,^{1–7} thermal,^{8,9} mechanical,³ and optical properties,¹⁰ have been studied, in which conventional LLDPE produced by Ziegler-Natta catalysts was used. It is, however, well known that the conventional LLDPE has broad molecular weight distribution and short chain branching distribution, which strongly affect the miscibility and/or compatibility with other polyolefins.^{11–15} Therefore, the studies used a well characterized LLDPE, such as the LLDPE produced by metallocene catalysts, are desired in an attempt to obtain further information on the

effect of the molecular architecture on the structure and properties for the LLDPE-LDPE blends. Recently, Lee et al.¹⁶ have investigated the miscibility of LDPE and LLDPE (ethylene-1-octene copolymer) produced by the metallocene catalyst, which has narrow molecular weight distribution and uniform comonomer incorporation. They showed that the LLDPE, in which the density is 919 kg m^{-3} , is miscible with LDPE in the amorphous region. Furthermore, they clearly showed that the two polymers exclude one another during crystallization. To our knowledge, however, systematic studies on the effect of the species and contents of the α -olefin unit in LLDPE on the structure and/or the properties for the blends have not been performed yet. In particular, the blends, in which very low density LLDPE (below 905 kg m^{-3}) is used, have not been studied, although they are attractive materials from the industrial point of view.

The aim of this study was to elucidate the structure and properties for the binary blends of LDPE and ethylene-1-hexene LLDPE with lower

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density (900 kg m^{-3}) by means of rheological and thermal measurements. Furthermore, the mechanical properties, such as tensile properties and hardness of the blends, were also examined.

EXPERIMENTAL

Materials and Blend Preparation

LLDPE used was an ethylene-1-hexene copolymer produced by a metallocene catalyst.^{17,18} The number- and weight-average molecular weights of the LLDPE were $M_n = 3.7 \times 10^5$ and $M_w = 6.9 \times 10^5$, respectively. LDPE used was a commercial grade (Petrocene 360, TOSOH Corp., Japan). The M_n and M_w were 7.0×10^4 and 6.6×10^5 , respectively. The species and contents of branches were determined by ^{13}C nuclear magnetic resonance (^{13}C -NMR) spectroscopy. The LLDPE has 18.6 of butyl branches/1000 backbone carbon atoms and the LDPE has 7 butyl, 2 pentyl, and 5 long ($>\text{C6}$) branches/1000 backbone carbon atoms.

The LLDPE and the LDPE were blended with a small amount of 2,6-di-*tert*-butyl-4-methylphenol as an oxidation inhibitor in a two-roll mill in which the surface temperature was kept at 423 K. The compositions of components in the LLDPE-LDPE blends were 100/0, 97.5/2.5, 95/5, 90/10, 80/20, 70/30, 50/50, 20/80, and 0/100 (w/w). The samples were melt pressed in a laboratory hot press at 473 K and 10 MPa for 15 min and then quenched at 303 K. The thickness of the compression-molded samples was adjusted to suitable thickness for measurements.

Measurements

Rheological properties in the molten state were measured using a cone-plate type rheometer (MR-500, Rheology Co., Ltd., Kyoto, Japan). The angular frequency dependence of shear storage modulus G' and loss modulus G'' at temperatures between 403 and 503 K was measured in the angular frequency range of 6.28×10^{-2} to $1.34 \times 10^1 \text{ s}^{-1}$. The time-temperature superposition was applied to frequency dependence of oscillatory moduli at different temperatures. The shift factor a_T was determined in the process of superposition. Shear rate dependence of shear viscosity η and primary normal stress coefficient θ were also measured at 463 K. It is well known that the rheological properties for LDPE are influenced by the processing condition, which is called "shear

modification."¹⁹⁻²¹ If the samples "remember" the shearing history, the rheological properties would depend on the annealing time before measurements. In this study, however, it was confirmed that the rheological properties are independent of the annealing time before the measurements.

Differential scanning calorimetry (DSC) measurements were performed using a Perkin-Elmer DSC-7. The samples of about 10 mg weight sealed in aluminum pans were heated from 300 to 500 K at a scanning rate of 10 K min^{-1} , annealed at 500 K for 5 min, and then cooled to room temperature at a rate of 10 K min^{-1} under a nitrogen atmosphere.

Density was measured using a water-isopropanol density-gradient column at 296 K.

The hardness, the resistance to indentation, was measured following the ASTM D 2240 standard method at room temperature and expressed in shore C.

Uniaxial tensile tests were performed using a tensile testing machine (TENSILON UTM-2.5T, Toyo Baldwin Co., Ltd., Tokyo, Japan) at 296 K. The stress was determined by dividing the tensile load by the initial cross-sectional area, and the strain was calculated from the ratio of the increment of the length between clumps to the initial gauge length. The strain rate was 0.016 s^{-1} .

RESULTS AND DISCUSSION

Rheological Properties in the Molten State

Figure 1 exemplifies the master curves of shear storage modulus G' and loss modulus G'' for the LLDPE-LDPE (50/50). The reference temperature is 463 K. Over the range of interest, the results for all samples were found to obey the principle of the time-temperature superposition.

The apparent activation energy ΔH_a can be calculated from the temperature dependence of shift factor a_T using the Arrhenius equation. Figure 2 shows the compositional dependence of ΔH_a . In general, ΔH_a of an LDPE is much larger than those of linear polyethylenes, such as high density PE (HDPE) and LLDPE.²²⁻²⁵ Graessley and Raju²⁴ showed that the activation energy increases with increasing the length of branches by their rheological measurements using hydrogenated polybutadienes with long chain branches. Assuming that the relationship between the length of branches and activation energy is applicable for the present study, the LDPE used is estimated to have long chain branches with 8.5

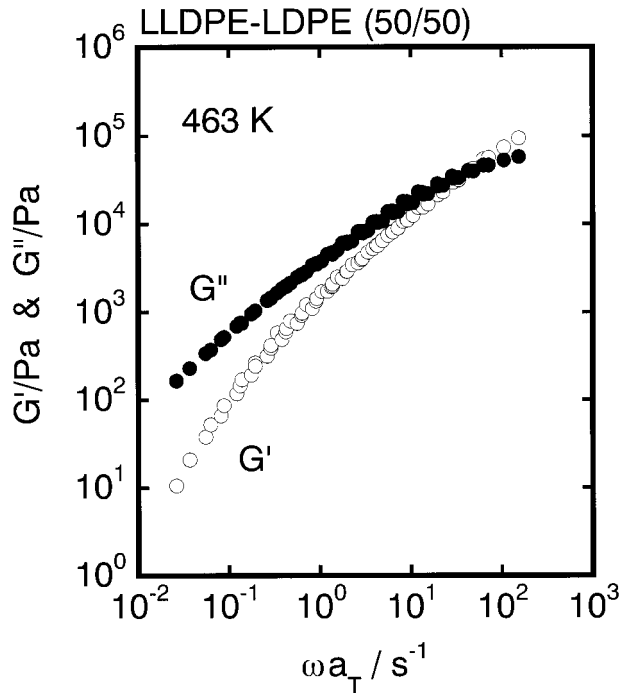


Figure 1 Master curves of frequency dependence of shear storage modulus G' (○) and loss modulus G'' (●) for LLDPE-LDPE (50/50) at 463 K.

$\times 10^4$ of molecular weight on the average. Furthermore, as is seen in Figure 2, ΔH_a increases monotonically with increasing the LDPE content.

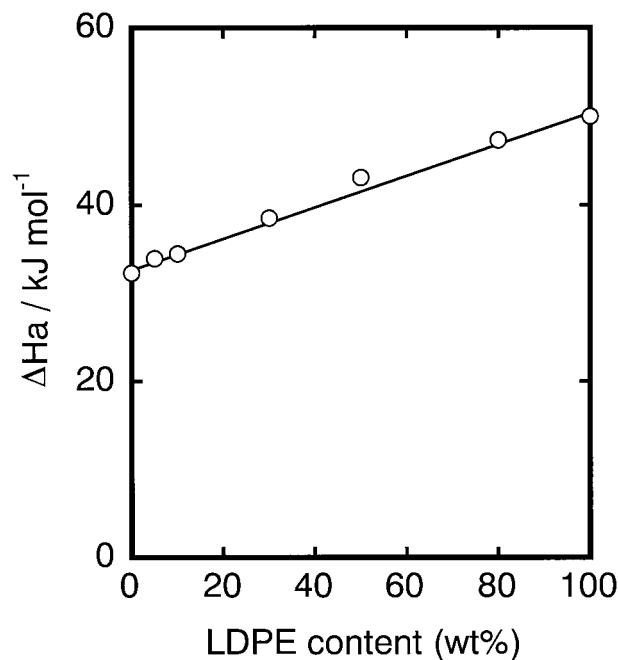


Figure 2 Compositional dependence of apparent activation energy ΔH_a .

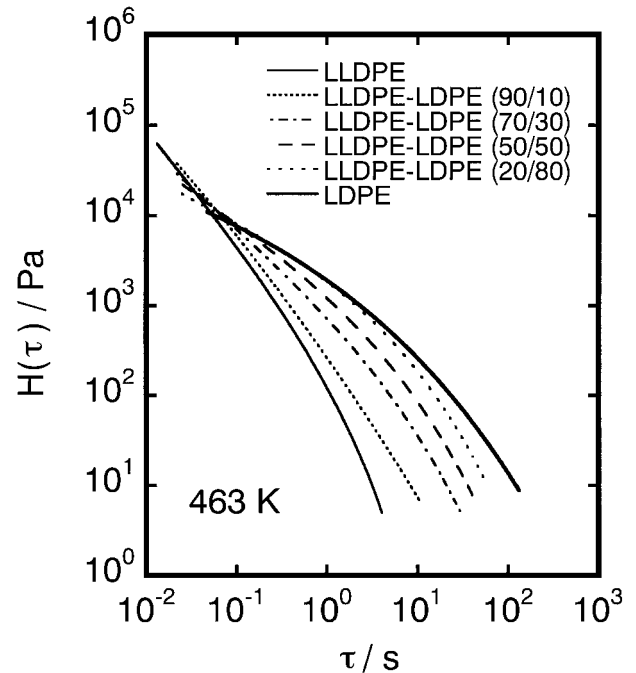


Figure 3 Relaxation spectra $H(\tau)$ for LLDPE, LDPE, and their blends at 463 K.

According to Graessley and Raju,²⁴ in miscible blends of linear and branched materials, the increment of the activation energy is proportional to the volume fraction of the branched polymer, which corresponds well to the present result. Moreover, following the WLF scheme, ΔH_a at high temperatures is related to the thermal expansion coefficient of free volume, that is, the linear additivity of free volume fraction is assumed for the blends.

Figure 3 shows the relaxation spectra $H(\tau)$ for the LDPE, the LLDPE, and their blends. The $H(\tau)$ is determined from the master curve of frequency dependence of G' using the Tschoegl equation,²⁶ which agrees well with those from G'' (but not presented here). As seen in Figure 3, the broader relaxation spectrum of the LDPE is evident from the more gradual decrease in spectrum, which is attributable to the broader molecular weight distribution and the existence of long chain branches. Furthermore, the spectra of the blends are intermediate between those of the individual pure components. It should be noted that there is no evidence of the long-time relaxation due to heterogeneous structure, suggesting that the longest relaxation mechanism of the blends is the entanglement slippage.

The shear rate $\dot{\gamma}$ dependence of shear viscosity η and primary normal stress coefficient θ is shown

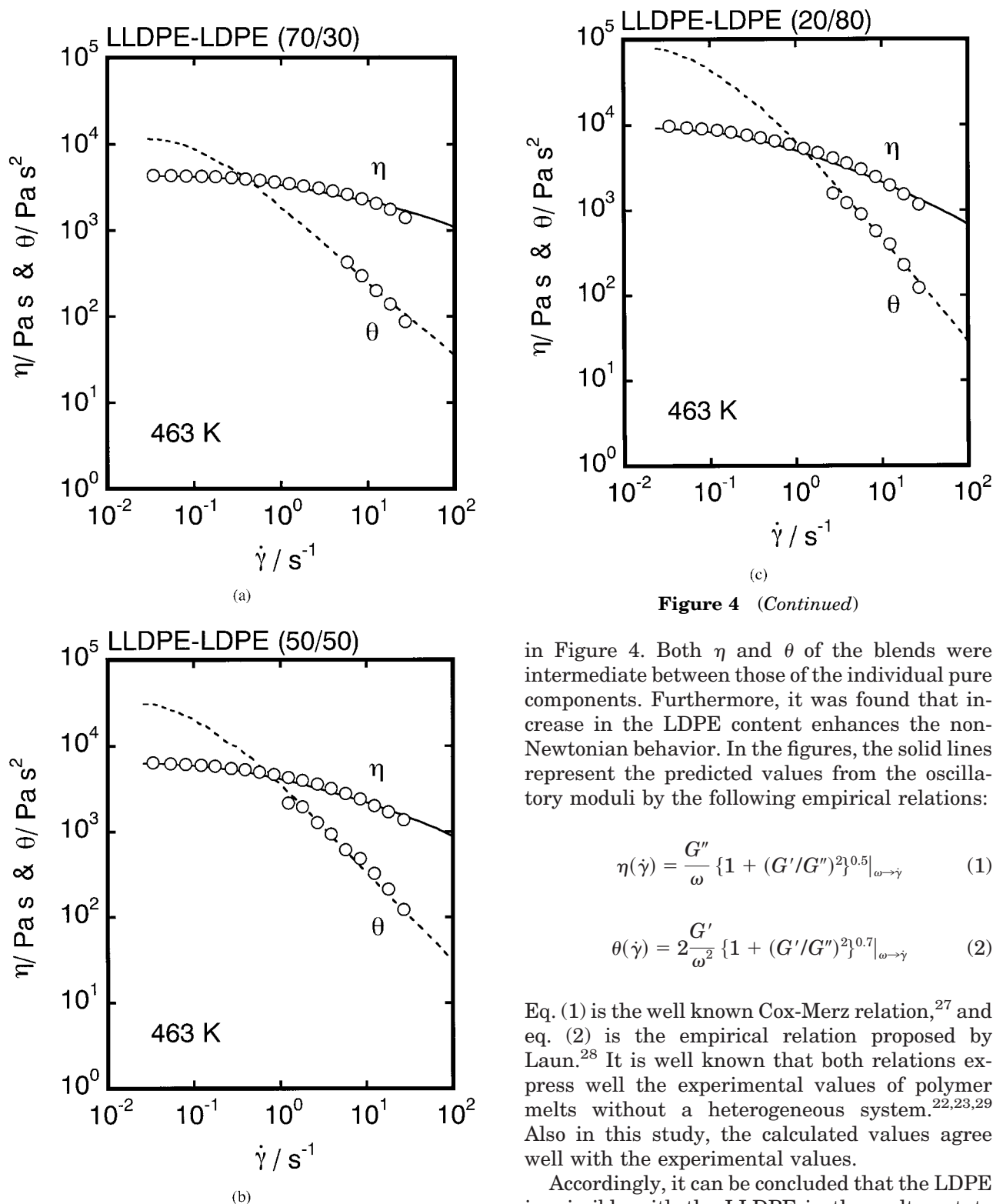


Figure 4 Shear rate dependence of shear viscosity η and primary normal stress coefficient θ for (a) LLDPE-LDPE (70/30), (b) LLDPE-LDPE (50/50), and (c) LLDPE-LDPE (20/80) at 463 K. In the figure, the solid and dashed lines represent the predicted values from eqs. (1) and (2), respectively.

Figure 4 (Continued)

in Figure 4. Both η and θ of the blends were intermediate between those of the individual pure components. Furthermore, it was found that increase in the LDPE content enhances the non-Newtonian behavior. In the figures, the solid lines represent the predicted values from the oscillatory moduli by the following empirical relations:

$$\eta(\dot{\gamma}) = \frac{G''}{\omega} \{1 + (G'/G'')^2\}^{0.5} \Big|_{\omega \rightarrow \dot{\gamma}} \quad (1)$$

$$\theta(\dot{\gamma}) = 2 \frac{G'}{\omega^2} \{1 + (G'/G'')^2\}^{0.7} \Big|_{\omega \rightarrow \dot{\gamma}} \quad (2)$$

Eq. (1) is the well known Cox-Merz relation,²⁷ and eq. (2) is the empirical relation proposed by Laun.²⁸ It is well known that both relations express well the experimental values of polymer melts without a heterogeneous system.^{22,23,29} Also in this study, the calculated values agree well with the experimental values.

Accordingly, it can be concluded that the LDPE is miscible with the LLDPE in the molten state from the rheological point of view.

Thermal Properties

Figure 5 shows the DSC melting thermograms for the sample films. It should be noted that the

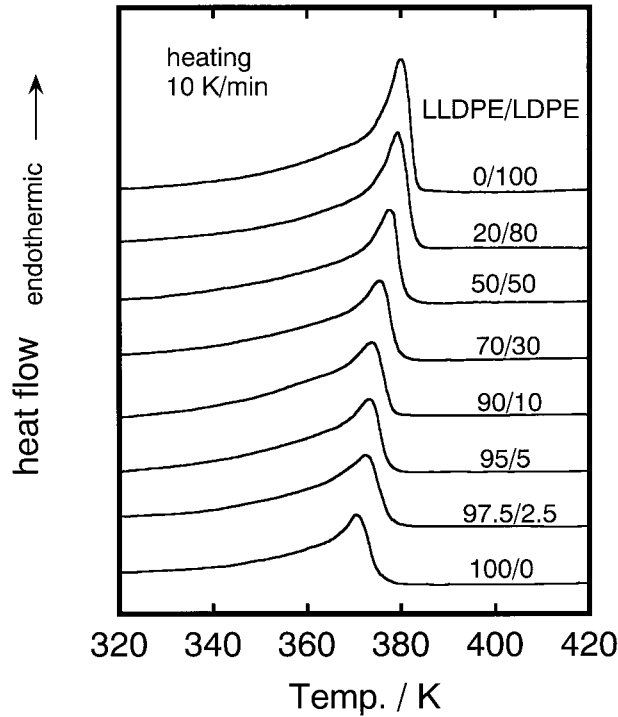


Figure 5 DSC melting thermograms for the sample films of LLDPE, LDPE, and their blends. Heating rate is 10 K min^{-1} .

melting peak of the LLDPE is lower than that of the LDPE, which is because of a large number of short chain branches in the LLDPE. Furthermore, only a single melting peak is observed in each blend irrespective of blend composition. The melting peaks and heat of fusion of the blends are intermediate between those of the individual pure components. Figure 6 shows the compositional dependence of melting temperature T_m and heat of fusion Δh_F . As seen in the figure, it is prominent for the LLDPE-rich blends that melting temperature and heat of fusion increase rapidly with increasing the LDPE content, indicating that the LDPE enhances the crystallization of the LLDPE from the molten state under the cooling condition used in this study. In an attempt to obtain further information on the crystallization mechanism, the DSC cooling-run measurements were also performed. Figure 7 shows the DSC crystallization thermograms obtained at a cooling rate of 10 K min^{-1} . It is apparent from the figure that the blending of a small amount of the LDPE enhances the crystallization temperature.

The experimental results in Figures 5–7 indicate that the LDPE-rich crystals, which were formed before the crystallization of the bulk materials, act as the nucleating agent for the crys-

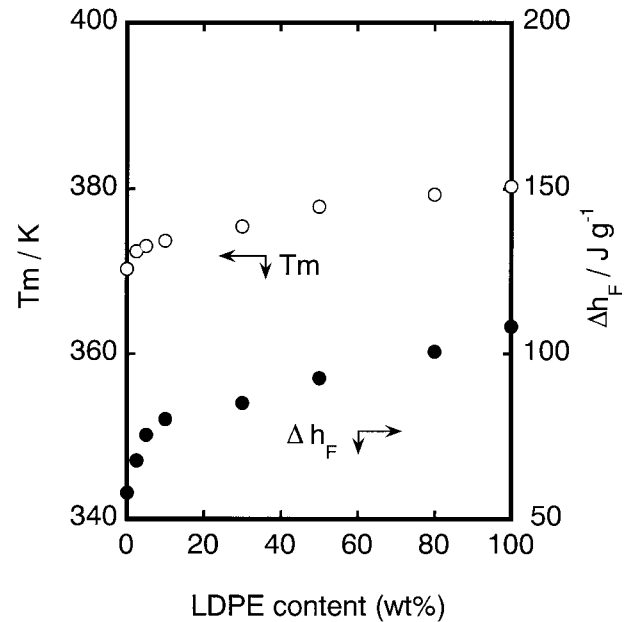


Figure 6 Compositional dependence of melting temperature, T_m , and heat of fusion Δh_F for the sample films of LLDPE, LDPE, and their blends.

tallization of the rest of the polymers. This suggests that the segregation of components takes place during the crystallization process. The seg-

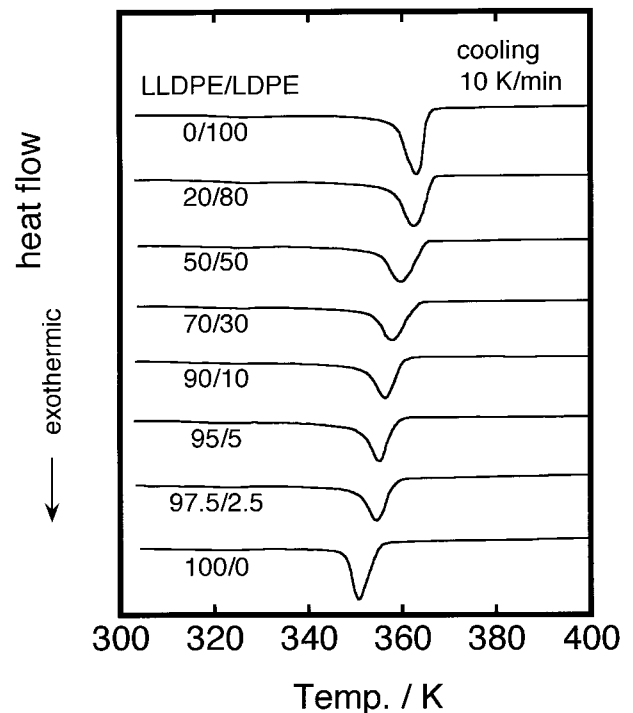


Figure 7 DSC cooling thermograms for LLDPE, LDPE, and their blends. Cooling rate is 10 K min^{-1} .

regation has been reported also by Müller et al.⁹ for the blends of LDPE and LLDPE produced by the Ziegler-Natta catalyst.

Figure 8 shows the compositional dependence of volume fraction of crystallinity χ_v for the sample films, which is determined from the density using the following relation:

$$\chi_v = \frac{\rho - \rho_a}{\rho_c - \rho_a} \quad (3)$$

where ρ , ρ_a , and ρ_c represent the density of the sample, the crystalline part (1000 kg m^{-3}),³⁰ and the amorphous part (855 kg m^{-3}),³⁰ respectively. As seen in the figure, the degree of crystallinity increases with increasing the LDPE content in the blends. Furthermore, it is also found that the small addition of the LDPE enhances the crystallinity of the LLDPE.

Mechanical Properties

Figure 9 shows the compositional dependence of shore-C hardness at 296 K. The magnitude of the hardness increases to a great degree with increasing the LDPE content, which is prominent in the LLDPE-rich blends. These results correspond well with the degree of crystallinity, as shown in Figure

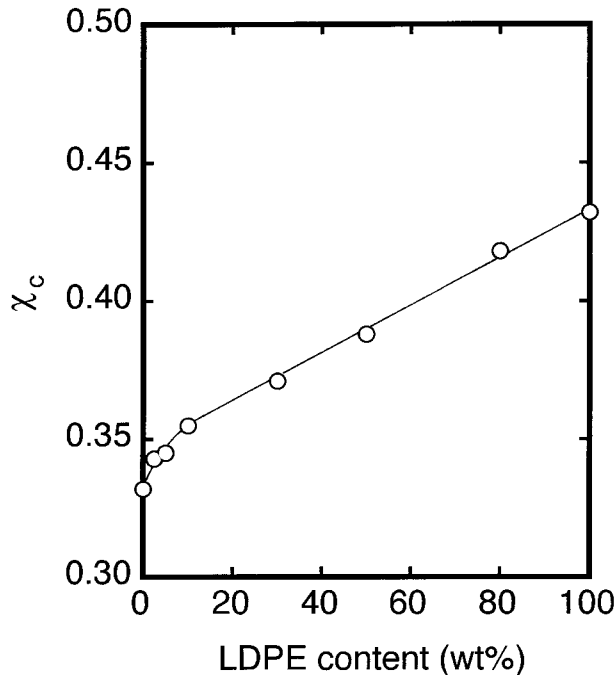


Figure 8 Compositional dependence of volume fraction of crystallinity χ_v for the sample films of LLDPE, LDPE, and their blends.

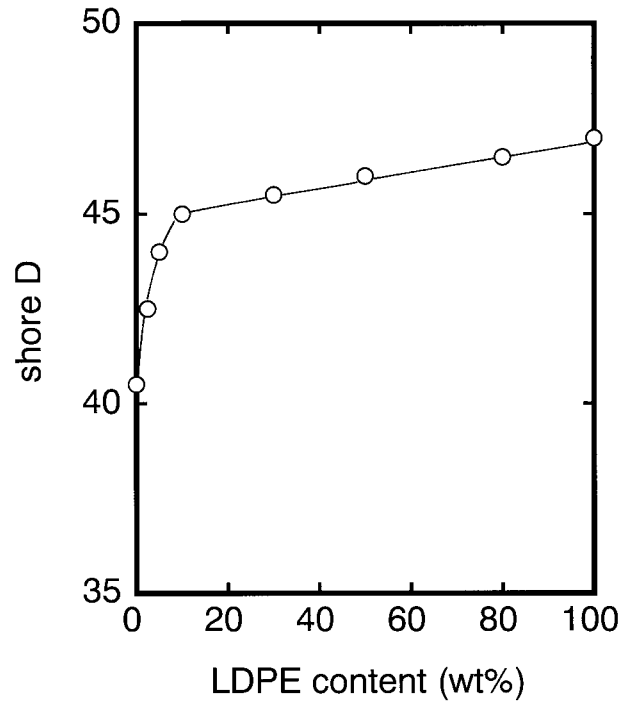


Figure 9 Compositional dependence of shore C hardness for the sample films of LLDPE, LDPE, and their blends at 296 K.

8. The fact indicates that the hardness of the blends is determined by the degree of crystallinity.

Uniaxial tensile testing was performed at 296 K. Figure 10 shows the compositional dependence

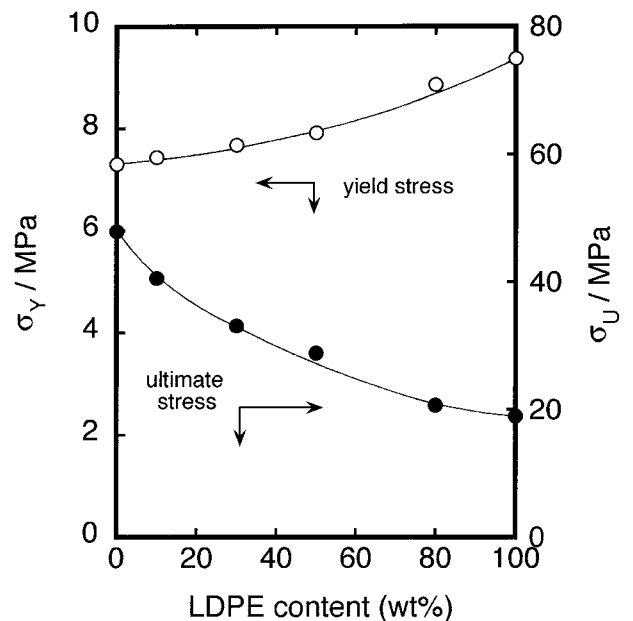


Figure 10 Compositional dependence of yield stress σ_y and ultimate stress σ_U for the sample films of LLDPE, LDPE, and their blends at 296 K.

of the yield stress (σ_Y) and ultimate stress (σ_U) at break point. As seen in the figure, the yield stress increases with increasing the LDPE content, although the ultimate stress decreases monotonically with increasing the LDPE content. The increase in the yield stress is attributed to the increase in the degree of crystallinity. Furthermore, a necking band appears and then extends beyond the yield point for all samples. This cold drawing process takes place under an approximate constant stress. Finally, the load increases up again to the break point, which is owing to the recrystallization of polymer chains because of the high degree of molecular orientation.^{31,32} The LDPE and the LLDPE-LDPE (20/80), however, show little increment of the load just before the break point, which is attributed to the prevention of the recrystallization because of the long chain branches. As a result, the ultimate stresses are lower than those of the LLDPE and the LLDPE-rich blends. Details of the tensile properties will be discussed in the following article.

CONCLUSIONS

The rheological, thermal, and mechanical properties for the binary blends composed of LLDPE and LDPE were studied. The LLDPE used is produced by the metallocene catalyst, and the density is lower than those of conventional LLDPEs produced by Ziegler-Natta catalyst. It was found by the rheological measurements that the LLDPE is miscible with the LDPE in the molten state. Apparent activation energy increases monotonically with increasing the LDPE content. The steady-state rheological properties of the blends can be predicted by the empirical relations using the oscillatory shear moduli. Furthermore, the LDPE is found to act as the nucleating agent for the crystallization of the LLDPE. As a result, blending a small amount of the LDPE into the LLDPE much enhances the degree of crystallinity, melting temperature, and hardness. It was also found that the ultimate stress decreases with an increase in the LDPE content, although the yield stress increases with an increase in the LDPE content.

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